

# Structure evolution of Pd-Ta-H alloy In Edwards' thermodynamics representation

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## Abstract

X-rays diffraction pictures time dependence of deformed alloy Pd-Ta being charged with hydrogen has been shown to be possibly caused by multi-pits character of energetic relief in the states space. Phenomenological model representing alloy structural evolution as a occasional roaming on minima of internal energy of non-ergodic system, has been offered in Lorenz synergetic scheme frames. Here, order parameters are the part of minima occupied by the system, conjugated field is considered to be Edwards entropy and control parameter is taken to be internal energy. Thermodynamics interpretation of Pd-Ta-H alloy evolution structure as a complex non-ergodic system is offered

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## 1 Introduction

The main object of statistics physics has lately become complex non-ergodic systems - spin and structural glasses, non-ordered heteropolymers, granulated matter, transportation flow, etc (see [1]). The main peculiarity of such systems is phase space separated into isolated regions with every region representing meta-stable thermodynamic state and their number  $N_0$  exponentially exceed full number of quasi particles  $N \rightarrow \infty$ ,  $N: N_0 = \exp(sN)$ , where  $s$  is so-called Edwards entropy respective to every complexity [2, 3]. Unlike Bolsman's measure describing disorder in given statistics ensemble, Edwards entropy describes disorder in complex system states distribution on internal energy minima respective to statistics ensemble. Statistics ensemble's play the role of particles in complicated systems. The distribution on these ensembles is described with effective temperature  $T$  and entropy  $S$ , introduced by Edwards [3]. So, complicated system with  $T = 0$  is corresponding to granulated matter distributed eventually on all minima (flat distribution).

Edwards systems that have exponentially huge number of minima  $N \gg 1$ , give us an example which is opposite to ergodic systems where  $N_0 = 1$ . According to this, an intermediate case where the number of minima  $N_0$  is neither exponentially big nor equal to one is of great interest.

Deformed Pd-Ta alloys being electrolytically charged with hydrogen represents this example as it is shown below. Really, solid state material under the influence of strong deformation can go so far away from the equilibrium state that the self-organization effects acting in dissipative structure formation become essential [4, 5]. During hydrogen charging of metal its atoms create essential internal tensions that can lead the system into a non-equilibrium state as an external influence does. The researches of annealed Pd-W-H alloy [6] deformed Pd-Sm-H, Pd-Er-H, Pd-Mo-H and Pd-Ta-H alloys [7, 8, 9, 10, 11, 12, 13]

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show that the non-monotonous structure transformation of non-regular character can take place there. Using of synergetic models [6, 10] allows to explain the main features of these systems behavior. But these models give no explanation of peculiarities of Pd-Ta-H alloy structural evolution shown below (see also [12]). This paper is devoted to this problem solution.

## 2 Experimental data

The method of the investigations was described in details in [9, 10, 11, 12], so we point out only at the fact that the original charging of Pd-Ta deformed sample (7at.%Ta) has been done electrolytically for 15 minutes at current density of 40 mA/cm<sup>2</sup>. After relaxing for 176 hours, the sample has been charged for the second time for the same period of time at 80 mA/m<sup>2</sup>. X-Rays researches of diffraction maxima 220 311 were done with computerized diffractometer with using  $CuK_{\alpha 1}$  components of x-rays spectrum doublet. The diffraction maxima decomposition into components was completed with "Origin" program package taking into consideration Lorenz form of components [14, 15].

The led researches show that, after the hydrogen charging of Pd-Ta deformed alloy, regular displacement of diffraction maxima which represents the lattice getting bigger and after that smaller take place. During the relaxation, stochastic changes of diffraction maxima position, their broadness and symmetry appear. So does stochastic transformation of their form including appearance and disappearance of some picks. Diffraction curves and their decompositions received for 200 maxima after the secondary charging at the different moments of time are shown at the fig.1. They represent complex structure of diffraction picks and non-monotonous character of their changes with time. Actually, the diffraction maxima have the structure shown at the table here.

As a bell-like form of diffraction maxima reflects homogeneous phase, one can presume that such changes of diffraction pictures are consequences of phases mutual transformations accordingly to Pd, Ta and H atoms re-distribution over different regions of the system. These structural changes can be repeating but not periodic. On the other hand, different broadness of components and their non-monotonous time changes mean that this process is accompanied with non-monotonous defect structure evolution and elastic fields created by this evolution appearance. Along with essential difference between hydrogen binding energy with ideal and defect Palladium lattice [16], the existence of far-acting fields causes essentially non-equilibrium character of researched system [5]. As it is known from the theory of glass-like theory [1], it causes complicated energetic relief appearance in the phase space of non-equilibrium state. Character of this relief is defined by the original defect structure and alloy atoms distribution, that are formed by mechanical work up, regimes of hydrogen charging and following relaxation. The difference of time dependence for the 220 and 331 coherent scattering regions oriented differently to the surface of the sample points out to energy being passed from freedom degrees to others that can lead to diffusion flows turbulence [12].

## 3 Theoretical scheme

The non-monotonous structural changes discussed above can be explained with the preposition that Pd-Ta deformed alloy hydrogen charging leads to the set of meta-stable states appearance corresponding to different phases and defect structures. In this case, generalized system diffusion over internal energy minima in accordance with the pointed states leads to stochastic structural changes observed during the experiment.

To understand this phenomenon, one needs to take into consideration the non-monotonous character of evolution, which is not of periodic character. These changes remind of strange attractor behavior described with synergetic Lorenz scheme [17]. Earlier, using Lorenz scheme has allowed us to describe non-monotonous behavior of Pd-Er-H double-phased alloy [6]. While doing that, we parameterized the

system with value portion of phase enriched with Er, concentration of Er atoms there and Er atoms traps concentration in matrix.

This parameterization cannot be used in multi-phased Pd-Ta-H alloy where the situation is much more difficult. Facing this problem for the first time, using parameters generalized over all the phases or yielding the most typical one helps avoiding the necessity of many phases behavior description. But this way we could have lost the extremely important peculiarity of multi-phased Pd-Ta-H alloy evolution: not only value correlation of the phases but their number change with time. According to this, the problem of parameters choice for the synergetic model which tries to describe Pd-Ta-H system stochastic behavior becomes very important.

According with Ruelle-Takens theorem [18], non-trivial behavior of such system is observed if the number of parameterizing freedom degrees is over two. At phase transition, the system behavior is described with hydrodynamic mode and its amplitude represents order parameter defined with thermostat state. Self-organized (synergetic) system peculiarity is: not only thermostat's influence over the subsystem but also its influence over the thermostat is very important. This influence can be either direct or indirect. First of them is defined with conjugated field, the second one - with control parameter. So, for the alloys of ordered synergetic model, order parameter is in accordance with usual long range order parameter, conjugated field refers to difference between chemical potential of components and control parameter - to difference of unit cell knots population of different atoms [19] Usual dissipative regime of phase transition is realized if relaxation time for order parameter and conjugated field is much longer then it is for control parameter. Otherwise, stationery value of control parameter increasing over crucial value leads not to ordering of this system but to transforming into regime of strange attractor [20].

To explain non-monotonous change of Pd-Ta-H alloy we take into consideration the fact that hydrogen charging leads to internal energy complicated relief state formation in the space. This relief has many minima separated with barriers (multi-valley structure). This preposition usage explains critical slowing down of structural transformation in the Pd-H systems [21]. This slowing down is caused by the hierarchical portrait of the relief; big minima are overlapped with smaller ones, then the smaller minima are covered with the minima that are even smaller, etc. Because of that, during its evolution, system is enforced to fill the smallest minima first, starting to fill bigger and bigger minima up to the biggest one which describes the system as a whole subject.

As to the observed case, the consideration which is limited with a type of minima that are not essentially different from each other is enough for our purpose. We numerate them with index  $\alpha$  covering the set of numbers 1, 2,..  $N_0$ . As a result, the system evolution is described with probability of distribution over these minima  $p_\alpha$  changes. Defining of  $p_\alpha(t)$  time dependence requires Fokker-Planck equation to be solved which is very difficult [22]. However, for the preliminary stage, we consider the integral characteristics that describe the type of  $p_\alpha$  distribution and thermodynamical behavior of the system as a whole subject enough for investigation. We take parameters as following:

- Number  $N$  of internal energy minima where the system is situated at the moment (obviously, it describes a half of dispersion width for probability  $p_\alpha$  );
- Entropy of the system dispersion over those minima

$$S = - \sum_{\alpha} p_{\alpha} \ln p_{\alpha} \quad (1)$$

- Specific internal energy  $e_\alpha$  at given minimum  $\alpha$ , which defines the full value of the internal energy

$$e = - \sum_{\alpha} p_{\alpha} e_{\alpha} \quad (2)$$

We will use the relation  $n = N/N_0$  of number  $N$  of internal energy minima occupied by system and full number of minima in the system  $N_0$  as an order parameter. Then specific Edwards entropy  $s = S/N_0$

which defines disorder in the distribution over minima  $\alpha$  is described with conjugated field and internal energy density and acts as a control parameter.

For the phenomenological description of the system evolution, main parameters  $\frac{dn}{dt}$ ,  $\frac{ds}{dt}$ ,  $\frac{de}{dt}$  of velocity changes are to relate to their values  $n$ ,  $s$ ,  $e$ . Here, Lorenz system advantage is in its accordance to the simplest choice of Hamiltonian in the respective microscopic representation [5]. Linear Lorenz equation is

$$\frac{dn}{dt} = -\frac{n}{\tau_n} + g_n s, \quad (3)$$

where first part describes Debye's relaxation of  $n(t)$  value to  $n = 0$  with character time  $\tau_n$ ; second part which contains positive coefficient  $g_n$  describes number of internal energy minima occupied by the system at increasing of entropy  $s$  in the dispersion over those minima.

Unlike (3), equations describing velocities  $\frac{ds}{dt}$ ,  $\frac{de}{dt}$  contain non-linear parts that represent the influence of the subsystem over the thermostat, showing the feedback we have discussed before. Thus, the equation for entropy change is

$$\frac{ds}{dt} = -\frac{s}{\tau_s} + g_s n e, \quad (4)$$

where first part describes Debye's relaxation to  $s = 0$  with time  $\tau_s$ . In accordance to second principle of thermodynamics, non-linear part which contains positive coefficient  $g_s$  takes into consideration entropy  $s$  increasing because of system dispersion over less deep minima of internal energy.

Last of the required equations defines velocity of internal energy increasing.

$$\frac{de}{dt} = -\frac{e - e_0}{\tau_e} + g_e s n \quad (5)$$

Here, Debye's relaxation with character time  $\tau_e$  leading not to zero value of the internal energy  $e$  but to  $e_0$  defined by system position at the phase diagram and the alloy preliminary work up is taken into consideration. Non-linear part with positive coefficient  $g_e$  represents negative feedback meaning that the re-distribution over internal energy minima should lead to decreasing of its full value  $e$  because of the system transformation to deeper minima. It should be pointed out to a very important role of non-linear parts. Their competition describes self-organized system behavior: positive feedback in (4) causes entropy  $s$  increasing because of relation between relative number of minima  $n$  and internal energy  $e$ . Positive feedback in equation (5) describes internal energy  $e$  decreasing because of the correlation between the number of minima  $n$  and entropy  $s$ .

The system of differential equation (3)-(5) generally has no analytic solution. Using of non-dimensional values  $n$ ,  $s$ ,  $e$ ,  $t$  scaling them as shown below seems to be very suitable:

$$n_m = (\tau_s g_s)^{\frac{1}{2}} (\tau_e g_e)^{\frac{1}{2}}, \quad s_m = \frac{n_m}{\tau_n g_n}, \quad e_m = (\tau_n g_n)^{-1} (\tau_s g_s)^{-1}, \quad \tau_n. \quad (6)$$

As a result, the equations (3)-(5) appear to be

$$\frac{dn}{dt} = -n + s, \quad (7)$$

$$\tau \frac{ds}{dt} = -s + n e, \quad (8)$$

$$\Theta \frac{de}{dt} = (E - e) - sn, \quad (9)$$

where the non-dimensional parameters are entered

$$\tau = \frac{\tau_s}{\tau_n}, \quad \Theta = \frac{\tau_e}{\tau_n}, \quad E = \frac{e_0}{e_m}. \quad (10)$$

In adiabatic regime  $\tau, \Theta \ll 1$  the principle of hierarchic co-ordering takes place. In accordance with this principle, changes of conjugated field  $s(t)$  and control parameter  $e(t)$  follow order parameter  $n(t)$  changes [18]. In this case, left parts of the equations (8), (9) can be omitted and they lead to:

$$s = \frac{En}{1 + n^2}, \quad e = \frac{E}{1 + n^2}. \quad (11)$$

In accordance with thermodynamics principles, they mean that Edwards' entropy monotonously grows but internal energy falls down with phases number growing up. On the other hand, variable  $n$  excluding from the equalities (11) gives simple dependence of entropy on internal energy:

$$s = \sqrt{e(E - e)}. \quad (12)$$

Using the definition of the temperature

$$T \equiv \frac{\partial e}{\partial s}. \quad (13)$$

we get

$$T = -\left(1 - \frac{E}{2e}\right)^{-1} \sqrt{\frac{E}{e} - 1}. \quad (14)$$

It means that Edwards' temperature becomes negative in the interval of the internal energy values  $E/2 < e < E$  and the system is in the process of self-organization. Therefore, in accordance with definition (13) at  $T < 0$  every increasing of internal energy  $\delta e > 0$  leads to entropy decreasing  $\delta s < 0$ , i.e. to self-ordering.

Substitution of the first of the equalities (11) into equation (7) turns Lorenz' system into Landau-Khalatnikov equation.

$$\frac{\partial n}{\partial t} = -\frac{\partial W}{\partial n}, \quad (15)$$

where the role of the free energy is played by synergetic potential

$$W = \frac{1}{2}n^2 - \frac{E}{2} \ln(1 + n^2) \quad (16)$$

At little values of internal energy  $E$  which is saved by the system as a result of external influence, dependence  $W(n)$  monotonously increases with minima at  $n = 0$  and multi-phased state is not advantageous synergetically. However, exceeding over crucial value  $E = 1$  synergetic potential  $W(n)$  reaches minima at

$$n_0 = \sqrt{(E - 1)} \quad (17)$$

Therefore, dissipative process of the system relaxation into the state respective to the value  $n_0 \neq 0$  of relative number of the phases appears to be advantageous. During this process, Edwards' temperature (14) reaches stationary value

$$T_0 = -\frac{\sqrt{(E-1)}}{1-E/2}, \quad (18)$$

and, being negative at over-critical values  $E > 1$ , monotonously decreases with growing of the internal energy saved by the system in consequence of external influence.

The represented adiabatic regime  $\tau, \theta \ll 1$  reflects monotonous transition of the dissipative system into non-ergodic stationary state. As we are interested in non-monotonous behavior, we can make a conclusion that the character time  $\tau, \Theta$  ratio should not be small. If it happens, analytical investigation of Lorenz' system appears to be impossible but the analysis [20] show that the regime of strange attractor of the self-organizing system specific for the experimental situation is realized at the condition  $\Theta > \tau > 1$ . Thus, time of internal energy change should exceed respective values of entropy and number of minima occupied by the system. Obviously, it is realized in the experiment investigated [12].

Besides these limitations for the ratio of relaxation time, strange attractor existence requires execution of  $E > 1$  condition [20]. This means that the stochastic changes of the structure in consequences of system states re-distribution over the minima respectively to different phases are realized only at the condition that the value of the internal energy saved by the system in a result of external influence exceeds critical value  $e_m$  which is defined with the third expression of (6). It can be noticed, that the systems that have great value of positive feedback's linear constant  $g_n$  and non-linear constant  $g_s$  and long relaxation time  $\tau_n, \tau_s$  are predisposed to stochastic behavior.

## 4 Conclusion

The led analyses shows that the stochastic structure transformation is realized because of the competitive influence of order parameter over the conjugated field and control parameter of self-organizing system. In the case of multi-phased Pd-Ta-H alloy where the roles of two last parameters are played by specific value of entropy  $s$  and internal energy  $e$  this competition is supported with the basic thermodynamic equality:

$$f = e - Ts \quad (19)$$

where  $T$  - Edwards' effective temperature. This equality is a result of Edwards' temperature definition (13) and conjugated entropy definition.

$$s = -\frac{\partial f}{\partial T}, \quad (20)$$

One of us has shown recently [23] that the pointed definitions along with identity (19) - are originally from the simplest field scheme in the limitation of which self-organizing system behavior is parameterized with double-component fields of order parameter, conjugated field and control parameter. Here first components are reduced to the values used before-respective number of occupied minima  $n$ , entropy  $s$  and internal energy  $e$  of non-ergodic system. Second components represent generalized flows conjugated to the pointed values such as flow of the probability density  $\bar{q}$  re-distribution among minima of internal energy; thermodynamics force  $-\nabla f$  equal to gradient of free energy, taken with the opposite sign; temperature opposite gradient  $-\nabla T$ . These components change appears to be essential, if the system is at non-stationary state. Its example represents non-monotonous behavior of multi-phased Pd-Ta-H alloy.

Hopefully, the synergetic scheme offered here represents the variant of strongly non-equilibrium state systems thermodynamics theory and its development is far from being completed [24, 25].

According to the analysis shown above, kinematics condition of the system of non-monotonous behavior consists of internal energy changes and temperature gradient changes that exceed respective value of entropy and gradient of free energy as well as of minima occupied by the system and conjugated probability flow. This condition explains abnormally big values of time intervals where stochastic behavior appear. Dynamic condition requires entropy increasing to have essential influence over the increasing number of minima where the system is situated. On the other hand, it requires decreasing of internal energy as consequences of re-distribution in order to lead to essential increasing of the entropy itself. Obviously, these conditions are provided with the essential values of  $g_n$  and  $g_s$  parameters that are realized at not high barriers separating minima and low "rigidity" of the internal energy relief. Thus, thermodynamics condition is considered a requirement of strongly non-equilibrium state of the system. This state of the system is reached with preliminary work up of the system such as radiation, essential deformation, hardening, etc. For the Pd-Ta-H system being investigated this work up consisted of preliminary deformation and hydrogen charging that lead to elastic tensions that are about 10% of elastic module character value. Considering this reasoning, we can presume that the internal energy saved by the system is big, too.

Let's point out at two observations of general character. First one is- critical slowing down of the structural transformation found in the system Pd-H [21] can be also found in the Pd-Ta-H alloy considered here. Our preliminary data received after hydrogenation for several times confirms this presumption. This means that at the quantity of hydrogenations essential increasing, the considered above multi-valley structure which is represented with the same minima transforms into multi-leveled hierarchical structure of energetic relief, which leads to the system evolution slowing down. This slowing down was found by the authors of [21].

Second observation is about the data of multi-phased deformed Pd-Mo-H alloy where the non-monotonous structural changes that are analog to the ones considered above were found [26]. As for Pd-Ta-H regular displacement of diffraction maxima takes place. This process reflects the lattice parameters getting bigger and, after that, smaller in anisotropic way. During the following relaxation, stochastic changes of the diffraction maxima components number, their positions, their width and intensity occur. Using this data, one can conclude that the non-regular behavior of the strongly dissipative multi-phased system is a specific feature for the structural changes of the alloys after hydrogen charging.

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Time after the charging, h	1,0	3,5	6,0	11,0	25,5	28,0	30,5	33,0	73,5	97,0	148
Number of picks, N	4	2	4	2	5	1	4	2	4	2	2
Relative number of picks, n	0,8	0,4	0,8	0,4	1	0,2	0,8	0,4	0,8	0,4	0,4
Number of figure	a	b	c	d	e	f	g	h	i	j	k

Table 1: Time dependence of diffraction maxima (220) number

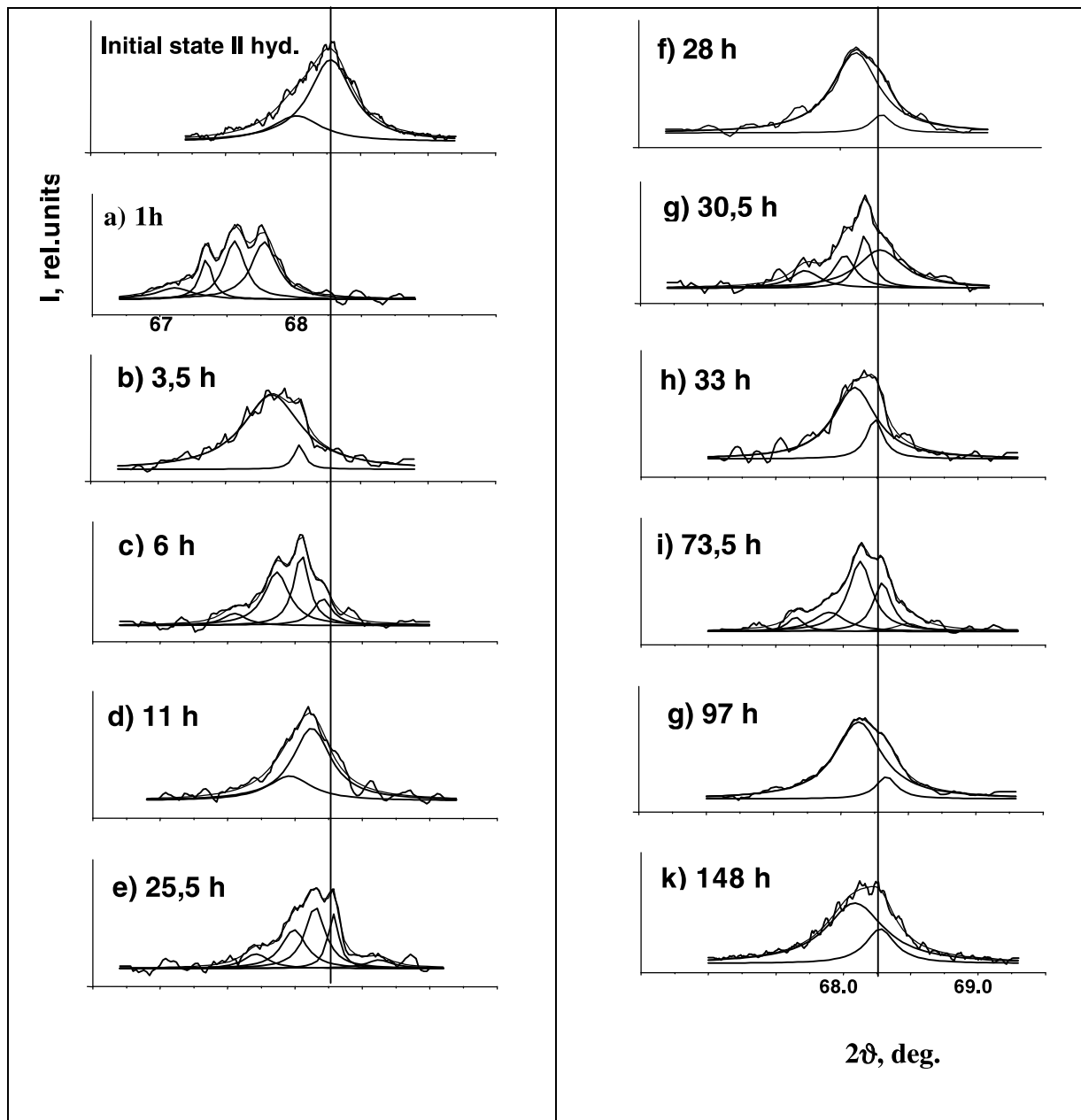


Figure 1: Time change of the position and profile of the diffraction line (220) after second charging: a) 1 h; b) 3,5; c) 6; d) 11; e) 25,5; f) 28; g) 30,5; h) 33; i) 73,5; j) 97,5; k) 148 (vertical line shows the position respective to original condition - 173 h of relaxation after second charging)